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16. ABSTRACT

The U. S. Environmental Protection Agency (EPA) has established quality assurance procedures for air pollution measurement systems. Among the areas of EPA's concern is the accuracy of compressed gas standards used for calibration and audits of continuous emission monitoring systems and ambient air quality analyzers. EPA's regulations specify that the certified values for these standards be traceable to National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) or to NIST/EPA-approved Certified Reference Materials via two traceability protocols. This article reports the results of an audit of all commercial gas manufacturers of sulfur dioxide, nitric oxide and carbon monoxide at ppm concentration levels. The article also shows how each gas manufacturer complied with the reporting requirements to the customers as stated in the traceability protocols.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Traceability, cylinder gas, sulfur dioxide, nitric oxide, carbon monoxide		

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Accuracy Assessment of EPA Protocol Gases in 1988

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The U.S. Environmental Protection Agency has established quality assurance procedures for air pollution measurement systems. These procedures are intended to reduce the uncertainty of environmental measurements. Among the areas of EPA's concern is the accuracy of compressed gas standards and liquid permeation standards used for calibration and audits of continuous emission monitoring systems and ambient air quality analyzers. EPA's regulations specify that the certified values for these standards be traceable to National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) or to NIST/EPA-approved Certified Reference Materials via two traceability protocols.[1-5] These protocols were published originally in 1978 and were revised in 1987. The revisions include the following items:

- Provision for analysis of compressed gas standards using dilution and ambient air quality analyzers;
- Provision for referencing liquid permeation devices to compressed gas standards;
- Extension of the certification period for the standards from 6 to 18 months in most cases;
- Additional documentation requirements for the standards' written certification reports; and
- Provision for periodic accuracy assessments of compressed gas standards and liquid permeation standards that are prepared and analyzed according to the protocols.

Research Triangle Institute (RTI) conducted an accuracy assessment of compressed gas standards in 1985 under contract to EPA.[6] Fifty standards were purchased from eleven specialty gas producers. These standards were specified to be prepared and analyzed according to the protocols. They were one of the following gas mixtures: sulfur dioxide (SO_2) in nitrogen (N_2) at 70 or 300 parts per million by volume (ppm), nitric oxide (NO) in N_2 at 70 or 400 ppm or carbon monoxide (CO) in air at 30 ppm. They were analyzed at RTI using SRMs as reference standards. Seventy percent of the producers' certified concentrations were found to be accurate to within plus or minus 2 percent and 94 percent of the concentrations were found to be accurate to within plus or minus 5 percent.

Following publication of the revised traceability protocols, EPA conducted an accuracy assessment of compressed gas standards in 1988. These standards were to be prepared and analyzed by specialty gas producers according to the revised protocols. The purposes of the assessment were : (1) to document the accuracy of the standards' certified concentrations; and (2) to check that the standards' written certification reports met the new documentation requirements. EPA directed RTI to purchase from all available sources and to analyze the following gas mixtures: 300 ppm SO_2 in N_2; 400 ppm NO in N_2; and 30 ppm CO in air.

Purchase of Compressed Gas Standards

A telephone survey indicated that eleven specialty gas producers market standards that are prepared and analyzed according to the protocols. These producers are as listed below:

- AGA Gas, Inc.;
- Airco Industrial Gases;
- Alphagaz Liquid Air;
- Big Three Industrial Gas, Inc.;
- Cryodyne Specialty Gases, Inc.;
- Linde (Union Carbide Corporation);
- Matheson Gas Products;
- MG Industries;
- National Specialty Gases;
- Scott-Marrin, Inc.; and
- Scott Specialty Gases.

Two anonymous third-party buyers purchased the standards to help ensure that gases of typical quality were obtained for the assessment. Standards were purchased from ten producers during January 1988. Standards were not purchased from AGA Gas because of procurement difficulties. The prices of the standards ranged from $253 to $480 with a mean price of $342. The buyers subsequently shipped the standards to RTI to be analyzed.

Upon receipt of the standards, the following irregularities were discovered:

- One buyer had ordered standards containing 30 ppm CO in N_2 rather than 30 ppm CO in air;
- Alphagaz had shipped a double order;
- The written certification reports indicated that only one of three Linde standards had been prepared and analyzed according to the protocols;
- The standards purchased from Cryodyne Specialty Gases and Matheson Gas Products had been prepared and

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Table I. Percent differences[a] between producer-certified concentrations and auditor-measured concentrations.

Specialty gas producer	300 ppm SO_2	400 ppm NO	30 ppm CO
Airco Special Gases	9.0%	−0.6%	0.8%[d]
Alphagaz (No. 1)[b]	5.7%	1.6%	0.4%
(No. 2)[b]	5.7%	2.0%	0.7%
Big Three Industrial Gas	2.5%	0.4%	1.1%
Cryodyne Specialty Gases[c]	2.5%	−0.4%	1.8%[d]
Linde (Union Carbide)	5.3%	0.2%[e]	−0.6%[e]
Matheson Gas Products[c]	3.9%	0.1%	4.3%[d]
MG Industries	6.4%	2.7%	0.9%[d]
National Specialty Gases	2.6%	1.0%	1.9%[d]
Scott-Marrin	1.2%	0.8%	−0.3%
Scott Specialty Gases	4.3%	−0.4%	−0.2%

[a] Percent Difference = $100\left[\frac{\text{certified conc.} - \text{measured conc.}}{\text{measured conc.}}\right]$

[b] Prepared and analyzed by MG Industries.

[c] Prepared and analyzed by National Specialty Gases.

[d] Balance gas for this standard is air. The balance gas for the remaining standards is nitrogen.

[e] This standard was not an EPA Protocol Gas.

analyzed by National Specialty Gases. However, their written certification reports did not indicate that National Specialty Gases produced these standards; and

- The standards purchased from Alphagaz had been prepared and analyzed by MG Industries. However, their written certification reports did not indicate that MG Industries produced these standards.

The revised protocols specify that the written certification reports must be signed by the analyst. They also specify that the reports must contain the identification of the laboratory where the standard was certified and the analyst who performed the certification.

MG Industries and National Specialty Gases may have inferred that an accuracy assessment was being conducted because of preparing and analyzing identical orders. They may have given special attention to the analysis of these standards.

RTI Analytical Procedures

Upon receipt of the standards, RTI measured the standards' pollutant concentrations with instruments using the following analytical principles: ultraviolet fluorescence for SO_2; chemilumenescence for NO; and nondispersive infrared photometry for CO. The standards were sampled without dilution through a stainless steel and Teflon™ sampling manifold. Sample flow through the manifold was controlled by stainless steel solenoid valves, a needle valve, and a digital timer. The voltage outputs from the instruments were recorded by a data logger with data averaging capabilities.

The reference standards for each set of measurements were two SRMs whose concentrations bracketed the concentrations of the standards that were being analyzed. For example, 100 and 500 ppm SO_2 SRMs were used in the analysis of the 300 ppm SO_2 standards. The linearity of the instruments' calibration curves was investigated by measurement of a zero gas and additional SRMs. The SO_2 data were corrected for the nonlinearity of the SO_2 instrument. The NO and CO instruments' calibration curves were found to be sufficiently linear such that the NO and CO data did not have to be corrected. The reference standards for the CO measurements contained the same balance gas as the standards being analyzed. The slope of the CO in air calibration curve was 1.4 percent greater than the CO in N_2 slope because of pressure broadening effects in the nondispersive infrared analyzer. This difference in the slopes was the motivation for the use of two different sets of carbon monoxide reference standards.

The pollutant concentration of each standard was measured at least three times. The mean measured concentration was compared with the producer's certified concentration. The relative standard deviation (RSD) for the replicate measurements was used as an index of measurement precision. The following mean RSDs were obtained for the instruments used in the assessment: 0.2 percent for SO_2; 0.4 percent for NO; and less than 0.1 percent for CO.

Results of Accuracy Assessment

The results of RTI's 1988 accuracy assessment are summarized in Table I. The accuracy of a producer's certified concentration is defined as the the percent difference between the producer's certified concentration and RTI's corresponding mean measured concentration. A frequency distribution for these results is given in Table II. In general, 64 percent of the results fell within the 0 to 2 percent range and 85 percent of the results fell within the 0 to 5 percent range. These 1988 results indicate a decline in accuracy in comparison with the results of the 1985 accuracy assessment of EPA Protocol Gases.[6] When only the standards containing 300 ppm SO_2, 400 ppm NO and 30 ppm CO are considered, 83 percent of the 1985 accuracies fell within the 0 to 2 percent range and 97 percent fell within the 0 to 5 percent range. The cause of this overall accuracy decline is the change in the accuracy of the 300 ppm SO_2 standards. Nine of ten 300 ppm SO_2 standards were accurate to within 5 percent in 1985. However, only six of eleven 300 ppm SO_2 standards were accurate to within 5 percent in 1988.

Any accuracy assessment is an instantaneous snapshot of the process being measured. These results should not be regarded as a final statement concerning the accuracy of EPA Protocol Gases. They can be used as an indicator of the current status of the accuracy of EPA Protocol Gases as a whole. However, individual results should not be taken as definitive indicators of the analytical capabilities of individual producers.

Table II. Frequency distribution for percent differences between producer-certified concentrations and auditor-measured concentrations.

Gas composition	Nominal concentration	Number of cylinders falling within a given range of absolute values of percent differences			
		0–2%	2–5%	5–10%	>10%
SO_2/N_2	300 ppm	1	5	5	0
NO/N_2	400 ppm	10	1	0	0
CO/N_2	30 ppm	6	0	0	0
CO/Air	30 ppm	4	1	0	0
Total		21	7	5	0

Table III. Required documentation for EPA protocol gases appearing on the producers' written certification reports.

Required documentation	Airco	Alphagaz	Big Three	Cryodyne	Linde	Matheson	MG Indust.	Nat. Spec.	Scott Mar.	Scott Spec.
Std. ID number	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Certified conc.	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Balance gas	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Cylinder pressure[a]	N	Y	Y	N	N	N	Y	N	Y	Y
Certification date	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Expiration date	Y	Y	Y	Y	b	Y	Y	Y	Y	Y
Ref. standard data[a]	Y	c	Y	c	b	c	c	c	Y	Y
Protocol statement[a]	d	Y	c	c	b	Y	Y	c	Y	c
Lab and analyst ID[a]	Y	e	Y	e	f	e	Y	Y	Y	Y
Gas analyzer ID[a]	c	Y	Y	c	c	c	Y	c	Y	c
All analyzer readings[a]	N	g	g	g	h	g	g	g	g	Y
Chronological record[a]	i	i	i	i	i	i	i	i	i	i
3 Significant digits[a]	Y	Y	Y	N	Y	N	Y	N	Y	Y
Cert. period (months)[a]	18	18	18	6	6[b]	6[j]	18	6	18	18

Y = Yes, N = No
[a] New documentation requirement.
[b] Only one of three Linde certificates listed this information.
[c] Incomplete information was given in the report.
[d] 1978 protocol was cited.
[e] Incorrect information was given in the report.
[f] Supervisory personnel, rather than the analyst, signed the report.
[g] Calculated concentrations, rather than analyzer readings, were given.
[h] Only one of three Linde cylinders were reassayed on a later date.
[i] Not applicable for the original certification of the standard.
[j] One of the three Matheson certificates listed an 18-month certification period.

NIST Confirmatory Analyses

Both RTI and EPA were concerned that the SO_2 results may have been biased because of some unknown error in RTI's analyses. As a result of this concern, one of the producers' SO_2 standards was sent to NIST for confirmatory analyses. NIST found that the SO_2 standard contained 326.0 ppm using an ultraviolet fluorescence instrument and 326.8 ppm using an electrochemical method. These values agreed to within 0.7 percent with RTI's measured value of 324.4 ppm. The good agreement between RTI's and NIST's analyses for this SO_2 standard suggests that RTI's other SO_2 concentration measurements were also accurate.

Documentation

An important part of the revised protocols is the requirement for additional information in the written certification reports. The producers' reports were reviewed to determine if the new documentation requirements were being followed. The results of this review are summarized in Table III. In general, all the reports met the 1978 documenation requirements. However, none of the reports met all the new 1987 documentation requirements. Some of the reports indicated that some producers were not aware of the revised protocol or had not implemented them yet.

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